Production and Characterization of Synthetic Jet Fuel Produced from Fischer-Tropsch Hydrocarbons

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The U.S. Military has initiated a project to evaluate jet fuel, produced from natural gas by processes developed by Syntroleum Corporation, for use in all military equipment capable of using either diesel fuel or jet fuel. A synthetic "Single Battlefield Fuel" would need to meet a wide range of specifications and in-use requirements before it would be accepted as a fuel by the military. The Syntroleum process for fuel production includes unique Autothermal Reforming of methane, reaction of the produced synthesis gas over cobalt catalyst to produce linear hydrocarbons of various chain lengths, and conversion of this feedstock into isoparaffinic fuel to meet the physical and chemical requirements per MIL-DTL-5624T for JP-5 Aviation Turbine Fuel. Syntroleum synthetic jet fuel produced for evaluation by DOD has an average carbon number of 13.2 and contains relatively little normal paraffins with proportionally lower normal paraffins at higher carbon numbers.

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PRODUCTION AND CHARACTERIZATION OF SYNTHETIC JET FUEL PRODUCED FROM FISCHER-TROPSCH HYDROCARBONS

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Introduction

Fuels derived from non-petroleum sources are being evaluated as replacement for petroleum-derived fuels by many organizations and countries. These fuels may come from tar-sands, shale oil, or natural sources. Many of the evaluations center on evaluation of the benefits of these fuels as replacement for crude oil derived fuels or their societal benefits versus the cost of production. Natural gas, with reserves having an energy equivalent approaching that of known crude oil reserves, represents a particularly attractive source of feed for future transportation fuel. Several companies are building, or will build, fuels production plants based on Fischer-Tropsch technology in several locations worldwide.

The U.S. Military has initiated a project to evaluate jet fuel produced from natural gas by processes developed by Syntroleum Corporation for use in all military equipment capable of using either diesel fuel or jet fuel. A synthetic "Single Battlefield Fuel" would need to meet a wide range of specifications and in-use requirements before it would be accepted as a fuel by the military. Syntroleum has produced fuel for evaluation by the Department of Defense under contract utilizing pilot plants located in Tulsa, Oklahoma. These fuels were produced to meet the physical and chemical requirements per MIL-DTL-5624T for JP-5 Aviation Turbine Fuel.[1] This paper documents the processes used to produce synthetic JP-5 from F-T paraffins obtained from Syntroleum's proprietary processes.

Synthesis of Paraffinic Hydrocarbon via the Fischer-Tropsch Reaction

Production of fuel from carbon sources via Fischer-Tropsch synthesis has three basic steps—synthesis gas generation, Fischer-Tropsch reaction, and hydroconversion. A typical conventional synthesis configuration is shown in Figure 1. The Fischer-Tropsch reaction produces a wide range of hydrocarbons with the distribution generally following the Anderson-Schlutz-Flory (ASF) equation. Olefins and oxygenated products are generally concentrated in the lower hydrocarbon range, with the majority of these species containing less than 20 carbon atoms. Alcohols identified in the reaction mixture are exclusively terminal, and olefins are a mixture of terminal combined with *cis*- and *trans*-2-olefins. The Fischer-Tropsch reaction products have been described in several publications and will not be discussed further here.

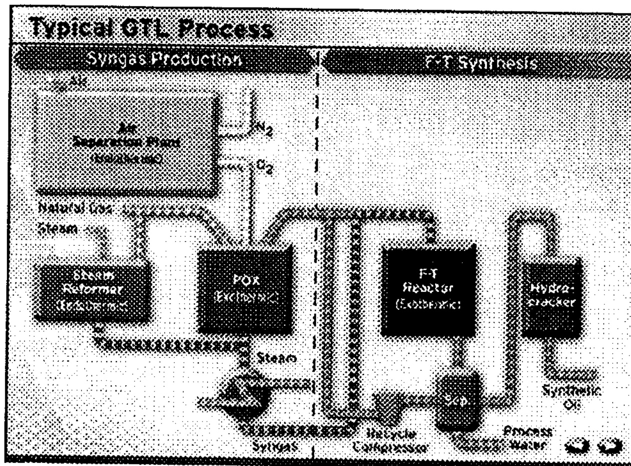

Figure 1. Conventional F-T synthesis configuration, including air separation unit, syngas generation, F-T reactor with recycle, and hydroprocessing.

Synthesis gas has been produced from many energy sources for well over 100 years. Depending on the carbon source and production technique, synthesis gas can vary in composition significantly. Several metals are active in the Fischer-Tropsch process, but the predominant metals currently under development are iron and cobalt. Iron offers an advantage in that synthesis gas of less than approximately 2:1 molar ratio hydrogen to carbon monoxide can be "shifted" to the ratio needed to produce paraffinic hydrocarbons via the water-gas shift reaction. Carbon dioxide is produced during the shift reaction. Cobalt offers advantages in stability, catalyst life, and reactivity over iron. Water produced during the F-T reaction tends to deactivate iron catalysts by production of inactive oxides.[2, 3]

Syntroleum has developed advanced technology that utilizes ambient air as the oxidant for syngas generation compared to most other processes that utilize nearly pure oxygen produced in cryogenic separation plants. Shown in Figure 2 is the Syntroleum synthesis process and how it compares to conventional process given in Figure 1. The Syntroleum Auto-Thermal Reformer (ATR) combines compressed air with methane and steam at high temperature over a nickel catalyst to produce 2.2:1 hydrogen to carbon monoxide. The process is exothermic and energy generated from this unit is used to power other processes in an integrated plant or used to produce power for export outside the plant boundary. The Syntroleum ATR is relatively unique in that the steam/carbon ratio is very low compared to commercial reformers resulting in higher overall reactor efficiencies. Energy considerations and more details have been discussed previously.[4]

The Cobalt catalyzed slurry phase Fischer-Tropsch processes have been under development for over 30 years.[5] Syntroleum has developed reactor systems to utilize nitrogen diluted synthesis gas that are substantially different form F-T

processes based on non-diluted synthesis gas. The cobalt-based slurry catalyst formulation is proprietary to Syntroleum.

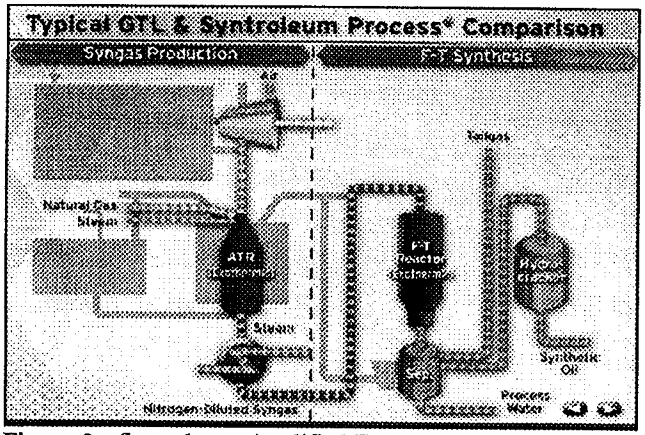

Figure 2. Syntroleum simplified F-T synthesis configuration with ATR and one reactor shown.

Production of Paraffinic Jet Fuel from Fischer-Tropsch Hydrocarbons

Fischer-Tropsch paraffins, including F-T wax, are predominantly linear normal paraffins with a small percentage of mono-methyl branched isoparaffins. The carbon distribution will vary based on reactor conditions and catalyst choices. The upper range of hydrocarbons will generally be above C60, with wax molecules having over 100 carbon atoms common for high ASF alpha products. These predominantly solid paraffinic products need to be isomerized to isoparaffins that are liquid at equipment operating conditions in order to be useful as fuel. Beginning in the 1940's, researchers have explored ways to convert F-T wax into fuel.

Moore et al[6] developed a process for conversion of normally solid paraffins, including FT wax, into normally liquid products utilizing modified Friedel-Crafts reagents and cracking suppressors. Waxy feeds are converted into branched isoparaffin products without substantial change in molecular weight. Both lubricants and diesel fuels were produced by this process. These authors reported that the effect of the reaction "is to increase the number of alkyl side chains of the normally solid hydrocarbons treated and that the products obtained consist essentially of branched chain hydrocarbons in which the alkyl side chains formed during the reaction consist substantially exclusively of methyl groups."

Moore[6] further reports that diesel fuel can be produced having a cetane number from 80 to 100 and the pour point of the product can be reduced to -60°C by controlling the isomerization of the product. This product in modern terms is of jet fuel quality, although at the time jet fuel was not well defined and specifications were just being defined.

Subsequent work by Good et al[7] improved this process by development of high temperature fixed bed catalytic reactors. This work, and contributions by a vast number of subsequent researchers, led to the current state of the art hydroprocessing technology. It is interesting to note that although the catalyst and process conditions have greatly changed over the years, the mechanism of reaction and reaction products are unchanged. Strong acid catalysts initiate the formation of carbenium ions in paraffinic hydrocarbons. These rearrange through what many believe are protonated cyclopropane intermediates to methyl-branched isoparaffins.

An example of this comes from the work of Benazzi et al[8], of the Institute Francais Du Petrole, where they hydroisomerized normal decane and normal heptadecane to obtain between 65% and 80% mono-methyl branched products and between 20% and 35% multi-methyl branched products. Many researchers in the hydroisomerization field, even now[9], routinely determine catalyst selectivity towards isomerization and cracking by experiments with pure normal paraffin feeds.

Production of Synthetic JP-5 from Syntroleum F-T Wax

The process developed by Syntroleum for production of distillate fuels such as diesel and jet fuel from Fischer-Tropsch products follows substantial prior art teachings including Egan and White.[10] Their work on wax hydrocracking processes showed that prior hydrotreatment of the feed greatly improved selectivity of the subsequent hydrocracking reaction. The Syntroleum process includes the following steps:

(1) Separation of light boiling fraction from the desired higher hydrocarbon fractions.
(2) Hydrotreatment of the feed to remove reactive species such as olefins and alcohols that may interfere with the hydrocracking process.
(3) Hydrocracking over a dual-functional catalyst incorporating a hydrogenation-dehydrogenation component and an acidic component.
(4) Distillation of the reactor effluent into product streams including naphtha and distillate fuels, and an under-converted heavy boiling fraction which is recycled to extinction.

Specific conditions for these reactions are proprietary to Syntroleum and will not be discussed here.

The jet fuel produced by this process has been fully characterized for chemical composition and assessed for conformance to the Military JP-5 specification. The chemical characterization is described here and a separate preprint paper summarizes the assessment of conformance to MIL-DTL-5624T.

Chemical Characterization of Syntroleum JP-5 Fuel

Characterization of the synthetic jet fuel known as Syntroleum S-5 included compositional and physical analyses per MIL-DTL-5624T to be sure that the fuel would meet this specification and similar specifications. Critical specifications for production of test fuel for the DOD contract, under which this program was conducted, are:

Distillation	Freezing Point	Hydrogen Content
Flash Point	Heating Value	Smoke Point
Density		

Other requirements in MIL-DTL-5624T are more related to fuel performance without and with required additives for JP-5; these are not addressed here. In addition to the testing per MIL-DTL-5624T requirements, detailed hydrocarbon analysis by gas chromatography and extensive analysis of hydrocarbon structure by ^{13}C and ^{1}H NMR were conducted.

Physical properties of jet fuel produced during a single run in the Syntroleum Tulsa Technology Center Refining Pilot Unit are shown in Table 1. These data indicated that Fischer-Tropsch wax can be hydroprocessed into distillate fuel substantially similar to the requirements for JP-5 fuel. This fuel will be further evaluated by DOD for conformance to "Fit for Purpose" requirements such a seal swell and turbine engine performance.

Table 1. Physical and Chemical Analysis of Syntroleum S-5 Synthetic Jet Fuel as Compared to MIL-DTL-5624T Requirements

Property	MIL-DTL-5624T	S-5 Batch 1 Lot 1
Color, Saybolt	Report	+30
Total Acid No., mg KOH/g	0.015 max	
Aromatics, vol %	25.0 max (D1319)	0.3
Total sulfur, mass %	0.40 max	<0.0001 (D5453)
Distillation-D86, °C		
IBP	Report	182
10%	206 max	195
20%	Report	202
50%	Report	228
90%	Report	
FBP	300 max	280
Flash Point, °C	60 min	62
Density, kg/L	0.788 min 0.845 max	0.767
Freezing Point, °C	-46 max	-50
Viscosity at -20°C, cSt	8.5 max	7.0
Heating Value, MJ/kg	42.6 min	44.1
Cetane Index	Report	62
Hydrogen, mass %	13.4 min	15.1
Smoke Point, mm	19.0 min	>43

Some compositional test methods called out in the specification, such as those for aromatic and sulfur content, are not appropriate for synthetic isoparaffinic fuels. More specifically, ASTM tests used in MIL-DTL-5624T were developed for hydrocarbon products derived from crude oils. These tests have acceptable use ranges that sometimes are not appropriate for synthetic products. One such example is ASTM D-1319, Hydrogen Types in Petroleum Products by Fluorescent Indicator Absorption, which is "limited to hydrocarbon types over a range of 5 to 99 volume % aromatics, 0.3 to 55 volume % olefins, and 1 to 95 volume % saturates..."[11] Results reported using D1319 are of limited accuracy for synthetic paraffinic products. Utilizing methods such as ASTM D5292, Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution NMR Spectroscopy[11], indicate less than the detectable levels of aromatics were present in the Syntroleum S-5 fuel.

Some results, such as Smoke Point by ASTM D1322, are outside the normal range of the test. The Smoke Point of Syntroleum S-5 is shown as >43. The actual value is beyond the range of the equipment used to measure smoke point for aviation fuels.

Additional analyses were made on the fuel provided to DOD to better characterize the chemical composition. Analytical GC data showed that the fuel contained relatively little normal paraffins with proportionally lower normal paraffins at higher carbon numbers. The average molecular weight for this fuel is 187.2 grams/mole, with an average carbon number of 13.2. The GC trace for this fuel is shown in Figure 3, and the Carbon Distribution is shown in Figure 4.

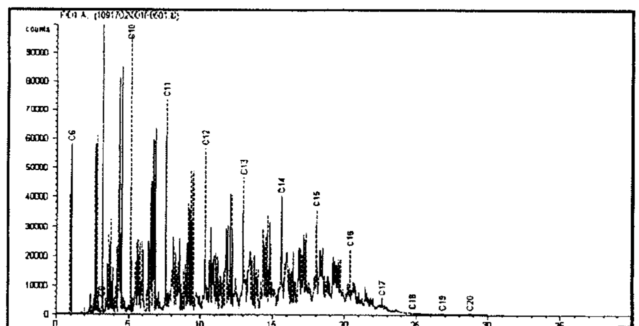

Figure 3. HP 5890 Analytical GC Trace of Syntroleum S-5 Synthetic Jet Fuel with Normal Paraffinic Hydrocarbons Labeled

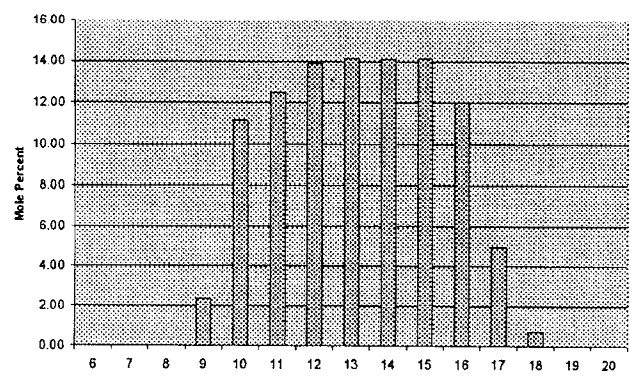

Figure 4. Paraffinic Hydrocarbon Distribution by Carbon Number for Syntroleum S-5 Synthetic Jet Fuel

Figure 5 shows the ^{1}H NMR of Syntroleum S-5 with high vertical expansion to illustrate the lack of olefinic or aromatic hydrocarbons. Utilizing 2x baseline noise as the limit of detection, the estimated aromatic proton content can be no greater than 0.05 % at this signal to noise level. Integration of the methyl and methylene regions coupled with molecular weight estimated by GC allows calculation of the extent of methyl branching. This sample of fuel contains approximately 1.7 methyl branches on each molecule.

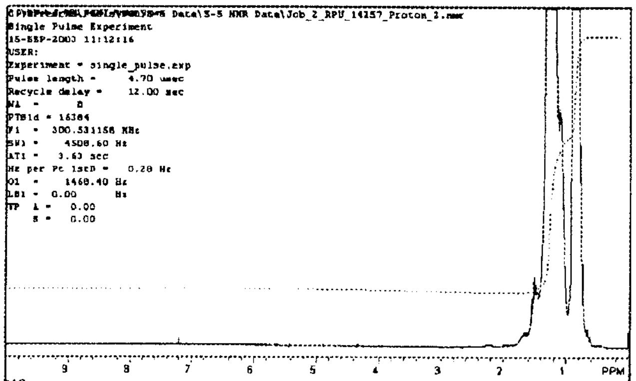

Figure 5. 300 mHz ^{1}H NMR Spectrum of Syntroleum S-5 Synthetic Jet Fuel with Vertical Expansion Showing Aromatic and Olefinic Regions

A ^{13}C NMR analysis of this fuel shown in Figure 6 confirms the high methyl branching content of the fuel with significant peaks at 22.6, 19.3, 19.7, and 19.5 ppm shift from TMS indicative of methyl branches at C2, C3, and C4 respectively. Branching beyond C4 is clustered in the 19.9 ppm region and individual peaks cannot be identified. The peak at approximately 11 ppm indicates the presence of a small amount of ethyl branched isoparaffin.

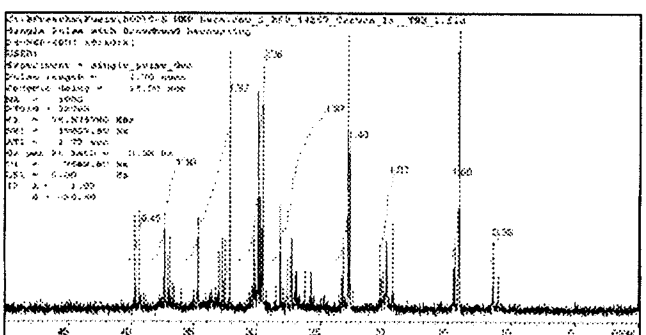

Figure 6. 75.57 mHz ^{13}C NMR of Syntroleum S-5 Synthetic Jet Fuel showing Paraffinic Region of Spectrum

Conclusions

Syntroleum S-5 synthetic jet fuel is a substantially isoparaffinic hydrocarbon product with undetectable levels of olefins, aromatics, sulfur, and other contaminants. S-5 fuel produced for evaluation by DOD has an average carbon number of 13.2 and contains relatively little normal paraffins with proportionally lower normal paraffins at higher carbon numbers. Physical properties of S-5 indicate that Fischer-Tropsch wax can be hydroprocessed into distillate fuel substantially similar to requirements for JP-5 fuel. This fuel is being evaluated for use in military applications by various organizations within DOD.

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